



(43) International Publication Date  
1 July 2004 (01.07.2004)

PCT

(10) International Publication Number  
**WO 2004/055114 A1**

- (51) International Patent Classification<sup>7</sup>: C08L 95/00, (74) Agent: KORTEKAAS, Marcel; KRATON Polymers Research B.V., Intellectual Property Services, P.O. Box 37666, NL-1030 BH AMSTERDAM (NL).  
E04D 5/02 // (C08L 95/00, 53:02)
- (21) International Application Number: PCT/EP2003/051005
- (22) International Filing Date: 15 December 2003 (15.12.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 02028216.6 16 December 2002 (16.12.2002) EP
- (71) Applicant (for all designated States except US): KRATON POLYMERS RESEARCH B.V. [NL/NL]; Badhuisweg 3, NL-1031 CM AMSTERDAM (NL).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): TROMMELEN, Erik A.T. [NL/NL]; KRATON Polymers Research B.V., Badhuisweg 3, NL-1031 CM Amsterdam (NL). DAMEN, Jacques W.M. [NL/NL]; KRATON Polymers Research B.V., Badhuisweg 3, NL-1031 CM Amsterdam (NL). van HEK, Jeffrey R. [NL/NL]; KRATON Polymers Research B.V., Badhuisweg 3, NL-1031 CM Amsterdam (NL).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BLOCK COPOLYMER MODIFIED BITUMENS, AND FELTS, COATINGS, SEALANTS AND ROADS MADE THEREFROM

(57) Abstract: The invention relates to thin block copolymer modified bituminous felts, comprising at least one block copolymer, comprising at least two poly(vinyl aromatic) blocks and at least one poly(conjugated diene) block, in a weight proportion of from more than 20 to 50 wt%, relative to the weight of the block copolymer and bitumen and optionally at least one filler, in a weight proportion in the range of from 0 to 50 wt%, relative to the weight of the complete composition and wherein the respective weight proportions of block copolymer, bitumen and filler add up to 100%. The invention also relates to the block copolymer modified bituminous composition, and the use thereof in bituminous pavements, coatings and sealants.

BEST AVAILABLE COPY

BLOCK COPOLYMER MODIFIED BITUMENS, AND FELTS, COATINGS,  
SEALANTS AND ROADS MADE THEREFROM

Technical Field

The present invention relates to block copolymer modified bitumens, to felts, coatings, sealants and roads made from said block copolymer modified bitumens, and the use of said felts for roofing and for application in construction and/or building industry, e.g. bridge deck layers and protective layers for concrete, steel and/or other constructions.

More in particular the present invention relates to block copolymer modified bitumens which comprise a block copolymer of vinyl aromatic and conjugated diene and to felts made from them which can be of a significant smaller thickness as compared to the conventional felts without affecting the felt's functional performance.

Description of Background Art

During the last two decades of the manufacture of block copolymer modified bituminous compositions, in particular for roofing, a clear trend has developed which aimed at using one or more block copolymers in bitumen, in actual weight proportions of up to 15 wt%, relative to the weight of the bitumen and block copolymer, while fillers were incorporated in actual weight proportions in the range of from 20 to 40 wt%, relative to the weight of the complete composition.

Such bituminous compositions were known from e.g. US patents nos. 4,405,680; 4,904,713; 5,051,457; 5,447,775; 5,308,676; 5,719,216; 5,854,335; 5,798,401 and 6,120,913.

As said block copolymers clearly formed and still form the most expensive elements of such modified bituminous

compositions, there was no incentive at all for economical reasons to look for significantly increased proportions of such block copolymers.

On the other hand a clear economical need has developed to provide roofing felts and other protecting felts in the building industry, which can be applied as sole single felt, which should be able to form a adequate barrier against water e.g. rain water or ground water, which moreover can contain increasing amounts of corrosive agents (securing water tightness) instead of the commonly applied multilayer systems, and which should not increase the weight of the complete construction and in particular roofs.

It is therefore an object of the present invention to provide block copolymer modified bituminous compositions and felts derived from them, which meet the hereinbefore mentioned conditions.

Another object of the present invention is the use of such block copolymer modified bituminous felts in building and/or engineering industry in an economically improved way.

A further object of the present invention is the use of said improved block copolymer modified bituminous compositions in bituminous pavements. The structural elements of a typical bituminous pavement comprises the pavement foundation (made of sub-grade, that is the natural soil of fill material, and sub-base, usually formed of good quality granular material); the road base, made of dense or open bituminous material, and the surfacing, comprising a base course and a wearing course. The load-carrying capacity of a pavement is a function of both the thickness of the material and its stiffness. The thickness of the base course therefore depends on the use of the pavement. It may vary from for instance 60 mm (cycle roads) to 180 mm

and more (heavily loaded roads). Replacing e.g. the bituminous composition used for the base course of the surfacing by the composition of the present invention, provides, in a manner similar to the bituminous felts, economically improved base courses that are about 2/3<sup>rd</sup> of the ordinary thickness, whilst providing a well shaped surface on which to construct the wearing course as well as to distribute the traffic loads over the road base.

#### Summary of the invention

As result of extensive research and experimentation, improved block copolymer bituminous compositions and felts and bituminous pavements derived from them, have surprisingly been found.

Accordingly, the invention relates to copolymer modified bituminous compositions, and felts as well as bituminous pavements derived from them, comprising at least one block copolymer, comprising at least two poly(vinyl aromatic) blocks and at least one poly(conjugated diene) block in a weight proportion of more than 20 wt% and more particular in the range of from more than 20 to 40 wt%, relative to the weight of the block copolymer and bitumen, and optionally at least one filler, in a weight proportion in the range of from 0 to 50 wt%, relative to the weight of the complete composition, and wherein the respective weight proportions of block copolymer, bitumen and filler add up to 100%.

#### Detailed description of the invention

The invention is hereafter discussed in respect of the use in bituminous felts in particular, although it is to be understood that the improvement may be found in bituminous pavements as well. The bituminous compositions may also be used in bituminous sealants and coatings.

With the term "thin", as used throughout the present specification, is meant that the block copolymer modified

bituminous felts or base courses of the present invention can have a thickness which is in average reduced by about 40% as compared to similar prior art bituminous felts or pavement component, while the relevant mechanical properties have been significantly improved into an excellent package.

More in particular the service temperature of said bituminous felts of the present invention have been found to be increased from e.g. 110°C to 170°C, the cold bend temperature has been found to be decreased from -30°C to -50°C or lower, while a high stiffness (walk-on-ability) was found in combination with an excellent low temperature flexibility.

It will be appreciated that such properties allow a substantial reduction in felt thickness without affecting the felt's functional performance requirements, i.e. sealing surfaces and securing water tightness.

This results in lower weight felts and potential significant economical advantages.

Moreover, the high level of copolymer modification will strengthen the service lifetime guarantee of critical performance indicators for protection against outside water, and in particular roofing applications.

It will be appreciated that the extra costs of the additional amounts of block copolymer in the bituminous compositions of the present invention will be much more than compensated by the surprisingly found advantages of the package of improved properties and the enabled use of significantly thinner felts.

As mentioned, similar advantages may be had when the composition is used in bituminous pavements, in particular the base course thereof, where reduction of thickness and increase in service temperature range is similarly appreciated.

The vinyl aromatic monomer to be incorporated into the block copolymer may be selected from styrene; o-methyl styrene; p-methyl styrene; p-tert-butyl styrene; 2,4-dimethylstyrene; alpha-methyl-styrene; vinyl naphthalene; vinyl toluene and vinyl xylene or mixtures thereof. A preferred vinyl aromatic monomer is styrene as substantially pure homomonomer or as main monomers, mixed with minor proportions (at most 10 wt%) of one or more of the other structurally related vinyl aromatic monomer(s) as specified hereinbefore, or with minor proportions of a comonomer (e.g. butadiene or isoprene). The use of substantially pure styrene is most preferred.

The conjugated diene monomer can be selected from butadiene; isoprene; 2,3-dimethyl 1,3-butadiene; 1,3-pentadiene, 1,3-hexadiene and mixtures thereof. Preferred conjugated diene comonomers are butadiene or isoprene or mixtures thereof. Said mixtures of butadiene and isoprene can be copolymerized into a central block, comprising individual homopolymer blocks of poly(butadiene) and poly(isoprene) or one sole substantially random copolymerized block, having average homopolymer block lengths of less than 100 monomer units and preferably of less than 20 monomer units. A more preferred conjugated diene comonomer is butadiene, which can be used as substantially pure comonomer alone (content more than 99%), or as main monomer, mixed with minor proportions (at most 10 wt%) of one or more of the hereinbefore specified structurally related conjugated diene monomer or with minor proportions of a vinyl aromatic comonomer such as styrene. The use of a substantially pure butadiene is preferred.

The block copolymers may be either linear or radial and will preferably have apparent total molecular weights in the range of from 40,000 to 500,000 and more preferably from 60,000 to 200,000.

It will be appreciated that the main linear triblock copolymers or radial block copolymers may also comprise relatively minor amounts of accompanying diblock copolymers, comprising the same poly(vinyl aromatic) block, and a poly(conjugated diene block) of an apparent molecular weight, being the half of the molecular weight of the central block poly(conjugated diene block) in a triblock and resulting from the manufacture of said triblock copolymer or radial block copolymer by coupling initially prepared living diblock copolymers with a coupling agent, as illustrated in e.g. US patents nos. 3,231,635; 3,251,905; 3,390,207; 3,598,887 and 4,219,627 and EP patent applications nos. 0413294A2; 0387671A1; 0636654A1 and WO 04/22931, the disclosures of which have been incorporated herein by reference.

The diblock content can be in the range of from 0 to 90 wt% and preferably from 0 to 35 wt%, and more preferably from 0 to 20 wt%, relative to the total weight of block copolymer(s).

The 1,2-addition during the polymerization of conjugated diene and preferably butadiene (vinyl content) is generally in the range of from 5 to 65 mole%, preferably in the range of from 8 to 45 and more preferably from 8 to 25 mole%.

The block copolymers may have bound vinyl aromatic monomer contents in the range of from 15 to 50 % and more preferably from 25 to 45 % and will have a linear triblock structure or radial structure (S-B-S or (SB)<sub>n</sub>-X). More preferred block copolymers are linear triblock (S-B-S) copolymers.

Examples of suitable block copolymers to be used according to the present invention are KRATON D1101, the road paving benchmark grade, KRATON D1102, a low molecular weight, linear block copolymer for a low melt viscosity,

KRATON D 1116 A radial, low styrene block copolymer for blends with a higher butadiene requirement, KRATON D1118, a high di-block containing granular polymer, also for use in combination with vulcanisation agents such as sulphur, KRATON D1186 and KRATON D1184, which are the main grades for roofing felts, KRATON D1192, a grade with lower PMB viscosity, high compatibility and good ageing performance, KRATON KX219 and KRATON KX220 block copolymers (KRATON is a registered trademark). In roofing felts also isoprene based styrenic block copolymers are used, to formulate self-adhesive felts. Block copolymers may be had from suppliers such as Polimeri Europa; Dynasol; Dexco; Fina; Chi Mei; Asahi; Taiwan Synthetic Rubber Company; Kumho; LCY and Yue Yang and others, that supply grades similar to the aforementioned KRATON grades.

It will be appreciated that the applied block copolymers may also have been selectively hydrogenated, which means that the poly(conjugated diene) central block(s) may have been fully or partially hydrogenated (residual unsaturation less than 25% of the original unsaturation), whereas the poly(vinyl aromatic) blocks have not been hydrogenated, e.g. as known from US patents nos. 3,113,986; 4,226,952; 5,039,755 and Reissue no. 27145, the disclosures of which are herein incorporated by reference.

The use of said hydrogenated block copolymers (S-EB-S or [S-EB]<sub>n</sub>-X) will provide as additional advantageous feature, that no protecting agent on the block copolymer modified bituminous felt upper surface will be necessary, such as slate chippings and the like.

Examples of said block copolymers are KRATON G1650, G1652 and G1654 block copolymers. Other suppliers include Dynasol, Kuraray, Asahi, and Taiwan Synthetic Rubber Company.



In preferred block copolymer modified bituminous compositions of the present invention, the weight proportion of block copolymers will be in the range of from more than 20 to 40 wt%, relative to the weight of the bitumen and block copolymer.

The bitumen can be selected from naturally occurring bitumens or bitumens derived from mineral oil. Also petroleum pitches obtained by a cracking process and coal tar can be used as the bituminous component, as well as blends of various bituminous materials.

Examples of suitable components include distillation or "straight-run bitumens". Precipitation bitumens, e.g. propane bitumens, blown bitumens, e.g. catalytically blown bitumen or "multiphalte", and mixtures thereof.

Other suitable bituminous components include mixtures of one or more of these bitumens with extenders (fluxes) such as petroleum extracts, e.g. aromatic extracts, distillates or residues, or with oils.

Suitable bituminous components (e.g. either "straight-run bitumens" or "fluxed bitumens") are those having a penetration in the range of from 10 to 350 dmm at 25°C (as measured according to ASTM D5, lower values indicate harder bitumen). In typical bituminous pavements, bitumens having a penetration in the range of from 40 to 150 dmm at 25°C are preferred. Depending on the climate and the intended use, in some base courses bitumen with a penetration down to 10 dmm may be used. On the other hand, in typical roofing felts bitumens are preferred that have a penetration in the range of from 100 to 300 dmm at 25°C.

It is the advantage of the present invention that now bitumens may be used that would normally be considered too hard. Accordingly, preferably quite hard bitumens of a penetration of from 10 to 100 dmm and more preferably from 30 to 80 dmm may be used.

The block copolymer modified bituminous compositions of the present invention may also comprise other ingredients that may be required due to the specific end-use envisaged.

Said other ingredients may be flame retarders, stabilizers, anti-statics, resins, oils, occurring in weight proportions in the range of from 0 to 15 wt%, relative to the weight of block copolymer and bitumen.

Fillers are included such as talc, calcium carbonate, carbon black fly ash, slate dust, limestone, dolomite and siliceous fillers such as clay, mica and other sheet silicates or mixtures of said fillers. In bituminous pavements, aggregate and sand is used.

The block copolymer modified bituminous compositions of the present invention may be prepared by various methods.

The block copolymer and bitumen can be blended at an elevated temperature, preferably not higher than 190°C for unhydrogenated block copolymers and not higher than 230°C for hydrogenated block copolymers, in conventional high shear blenders such as a ribbon blender, a drum mixer, where after the filler can be mixed in, wherein lower molecular weight block copolymers have been included.

For compositions wherein relatively higher molecular weight block copolymers have been included, blending of block copolymer with bitumen may be carried out by calendaring, in a Branbury internal mixer or any other means known to be used for blending high viscous compositions.

It will be appreciated that the block copolymer modified bituminous felts of the present invention will have a thickness of from 1 to 5 mm; preferably from 1.5 to 2.5 mm for roofing felts and from 2.5 to 3.5 mm for bridge deck layers.

Said modified bituminous felts may be applied as one single layer and are therefore significantly cheaper than conventional felts and/or multilayer systems.

The block copolymer modified bituminous felts of the present invention have a service temperature of from  $-35^{\circ}\text{C}$  or lower.

The new bituminous pavements may have base courses of about 40 mm thickness, whilst maintaining the properties of an ordinary base course of 60 mm thickness.

The following examples illustrate the present invention, however without restricting its scope to these specific embodiments.

#### Examples

Several block copolymers and bitumen grades were mixed in a SILVERSON LR2 high shear mixer in weight proportions as specified in the following table. The bitumen was heated to  $160^{\circ}\text{C}$  and subsequently the block copolymers were added. During polymer addition the temperature was kept under  $180^{\circ}\text{C}$ . Blending was continued until a homogeneous blend was obtained. A filler, if any, was added under mixing.

#### Conclusion

The block copolymer modified bitumen compositions of Examples I and III (vs. comparative Examples II and IV) exhibit an outstanding balance between high stiffness (low Pen at  $50^{\circ}\text{C}$ ) and excellent Low Temperature performance. This results in a superb Service Temperature range. Moreover, the novel compositions maintain their low Cold Bend property even if use is made of (cheap) filler. Examples V and VI demonstrate that the invention is not limited to a specific block copolymer of bitumen.

Although not demonstrated here, the new block copolymer modified bituminous compositions may be used in other end-uses as well

| <u>Example</u>                    | I   | II  | III (a) III (b) | IV (a) IV (b) | V   | VI  |
|-----------------------------------|-----|-----|-----------------|---------------|-----|-----|
| <u>Comparative Example</u>        |     |     |                 |               |     |     |
| Bitumen B45/60, %wt               | 75  | 88  | 75 75           | 88 88         | 75  | 75  |
| Bitumen PX-60 , %wt               |     |     |                 |               |     |     |
| Bitumen B-160 , %wt               |     |     | 35              | 35            |     |     |
| Filler, %wt on total              |     |     |                 |               |     |     |
| Block copolymer A, %wt            | 25  | 12  | 25 25           | 12 12         |     | 25  |
| Block copolymer B, %wt            |     |     |                 |               | 25  |     |
| <u>Properties of compositions</u> |     |     |                 |               |     |     |
| Softening point R&B, °C           | 140 | 112 | 139 139         | 110 111       | 112 | 145 |
| Pen at 25°C, dmm                  | 25  | 31  | 18 18           | 32 23         | 21  | 32  |
| Pen at 50°C, dmm                  | 48  | 96  | 44 44           | 104 87        | 50  | 63  |
| Cold Bend, pass °C                | -50 | -15 | -50 -50         | -30 -25       | -50 | -50 |
| DIN Flow, pass °C                 | 120 | 90  | 120 120         | 85 85         | 90  | 135 |
| Service temperature range, °C     | 170 | 105 | 170 170         | 125 120       | 140 | 185 |

The test methods used were:

- Viscosity: evaluated at 180°C using a Haeke roto-viscosimeter, using a shear rate of 20 s<sup>-1</sup> and 100 s<sup>-1</sup>
- Cold blend: according to UEAtc M.O.A.T. no. 31; 1984,
- Flow Resistance Temperature: according to DIN 52123; Aug. 1985,
- Softening point R&B: according to ASTM D36, corrected for stirring with +1.5°C,
- Penetration: at 25°C or 50°C according to ASTM D5-94.

The bitumen grades used for the listed examples were compatible bitumens:

- PX-60 bitumen is a mixture of 81 wt% of propane bitumen ex-Phillipines (Pililla, TMC no. 26260) +19 wt% of Bright Furfural Extract (BFE, aromatic oil/flux, TMC no. 24206), showing a penetration of 60 dmm at 25°C.
- B45/60 is a bitumen obtained by vacuum distillation of Venezuelan crude oil (in ESHA refinery, Amsterdam), having a penetration of 50 dmm at 25°C.
- B-160 is a bitumen obtained by vacuum distillation of Middle East crude oil supplied by SIPLAST (TOTAL), showing a penetration of 160 dmm at 25°C.

Block copolymer A is a triblock copolymer, comprising poly(styrene) blocks and a poly(butadiene) block, having a PSC of 31 wt%, a total molecular weight of 171,000, a vinyl content of 8 mole% and a coupling efficiency of 80%.

Block copolymer B is a triblock copolymer, comprising poly(styrene) blocks and a poly(butadiene) block, having a PSC of 29.5 wt%, a total molecular weight of 127,000 (measured by Gel Permeation Chromatography and expressed in terms of standard poly(styrene)), a coupling efficiency of 84% and a vinyl content of 8 mole%.

As filler was used either WIGRO 60K or Betocarb P2 limestone (WIGRO and Betocarb are trademarks).

## C L A I M S

1. Thin block copolymer modified bituminous felts, comprising at least one block copolymer, comprising at least two poly(vinyl aromatic) blocks and at least one poly(conjugated diene) block, in a weight proportion of from more than 20 to 50 wt%, relative to the weight of the block copolymer and bitumen and optionally at least one filler, in a weight proportion in the range of from 0 to 50 wt%, relative to the weight of the complete composition and wherein the respective weight proportions of block copolymer, bitumen and filler add up to 100%.
2. Thin block copolymer modified bituminous felts according to claim 1, wherein the weight proportions of block copolymer is in the range of from more than 20 to 40 wt%, relative to the weight of the block copolymer and bitumen.
3. Thin block copolymer modified bituminous felts according to claims 1 and 2, having a service temperature of from 140-200°C and a cold bend temperature of from -35°C or lower.
4. Thin block copolymer modified bituminous felts according to claim 1, wherein the block copolymer is a linear triblock copolymer S-B-S, optionally mixed with diblock S-B, wherein each S independently represents poly(styrene) and each B independently represents poly(butadiene) and wherein the diblock copolymer occurs in a weight proportion of from 0 to 35 wt%.
5. Thin block copolymer modified bituminous felts according to claim 1, wherein the bound poly(vinyl aromatic) content in the block copolymer is in the range of from 25 to 45 wt%.

6. Thin block copolymer modified bituminous felts according to claim 1, wherein the 1,2-addition in the conjugated diene polymerization is in the range of from 5 to 65 mole% and preferably from 8 to 45 mole%.
7. Thin block copolymer modified bituminous felts according to claim 1, having a thickness of from 1 to 5 mm, preferably from 1.5 to 2.5 mm if they are envisaged as roofing felts, or preferably from 2.5 to 3.5 mm if they are envisaged as bridge deck layers.
8. Thin block copolymer modified bituminous pavements, comprising at least one block copolymer, comprising at least two poly(vinyl aromatic) blocks and at least one poly(conjugated diene) block, in a weight proportion of from more than 20 to 50 wt%, relative to the weight of the block copolymer and bitumen and optionally at least one filler, in a weight proportion in the range of from 0 to 50 wt%, relative to the weight of the complete composition and wherein the respective weight proportions of block copolymer, bitumen and filler add up to 100%.
9. Block copolymer modified bituminous compositions, wherein the bitumen has a penetration value at 25°C (according to ASTM D5) in the range of from 10 to 350 dmm, and wherein the block copolymer occurs in a weight proportion in the range of from more than 20 to 50 wt%, relative to the weight of bitumen and block copolymer.
10. Use of thin block copolymer modified bituminous felts according to claims 1-7 for roofing and application in construction and/or building industry.

| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>IPC 7 C08L95/00 E04D5/02 //(C08L95/00,53:02)  |  |   |
|---|--|---|
| According to International Patent Classification (IPC) or to both national classification and IPC   |  |   |
| <b>B. FIELDS SEARCHED</b><br>Minimum documentation searched (classification system followed by classification symbols)<br>IPC 7 C08L E04D   |  |   |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched   |  |   |
| Electronic data base consulted during the international search (name of data base and, where practical, search terms used)<br>EPO-Internal, WPI Data, PAJ   |  |   |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>   |  |   |
| Category *  | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No.   |
| A   | EP 0 853 103 A (FINA RESEARCH)<br>15 July 1998 (1998-07-15)<br>claims 1,9  | 1-10  |
| A   | WO 02 26889 A (KRATON POLYMERS RES B V<br>;HEIMERIKX GERARDUS WILHELMUS J (NL);<br>TROM) 4 April 2002 (2002-04-04)<br>page 5, line 26-30; claims 1,22,24 | 1-10  |
| A   | WO 02 44281 A (KRATON POLYMERS RES B V<br>;BODT DUCO (NL); JONG WOUTER DE (NL);<br>TROM) 6 June 2002 (2002-06-06)<br>page 3, line 31-34; claims 1,8,9    | 1-10  |
| P,X   | EP 1 348 737 A (KRATON POLYMERS RES B V)<br>1 October 2003 (2003-10-01)<br>paragraph '0030!; claims 1,7,10,11  | 1-10  |
| <input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.  |  |   |
| <b>* Special categories of cited documents :</b><br><div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*Z* document member of the same patent family</p> </div> </div> |  |   |
| Date of the actual completion of the international search<br><br><div style="text-align: center; font-size: 1.2em;">12 March 2004</div>   |  | Date of mailing of the international search report<br><br><div style="text-align: center; font-size: 1.2em;">22/03/2004</div> |
| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax (+31-70) 340-3016   |  | Authorized officer<br><br><div style="text-align: center; font-size: 1.2em;">Hoffmann, K</div>                                |



| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|---|---|---------------------|----------------------------|---------------------|
| EP 0853103                                | A | 15-07-1998          | US 6008277 A               | 28-12-1999          |
|   |   |                     | EP 0853103 A1              | 15-07-1998          |
|   |   |                     | AT 204599 T                | 15-09-2001          |
|   |   |                     | CN 1249774 T               | 05-04-2000          |
|   |   |                     | DE 69801417 D1             | 27-09-2001          |
|   |   |                     | WO 9830635 A1              | 16-07-1998          |
|   |   |                     | EP 0953016 A1              | 03-11-1999          |
|   |   |                     | JP 2001507752 T            | 12-06-2001          |
|   |   |                     | NO 993336 A                | 07-09-1999          |
|   |   |                     | TW 495539 B                | 21-07-2002          |
|   |   |                     | US RE37581 E1              | 12-03-2002          |
| WO 0226889                                | A | 04-04-2002          | AU 1500202 A               | 08-04-2002          |
|   |   |                     | CA 2423787 A1              | 04-04-2002          |
|   |   |                     | CN 1473177 T               | 04-02-2004          |
|   |   |                     | WO 0226889 A1              | 04-04-2002          |
|   |   |                     | EP 1325082 A1              | 09-07-2003          |
|   |   |                     | NO 20031406 A              | 27-05-2003          |
|   |   |                     | US 2004014846 A1           | 22-01-2004          |
| WO 0244281                                | A | 06-06-2002          | AU 2960202 A               | 11-06-2002          |
|   |   |                     | CA 2432529 A1              | 06-06-2002          |
|   |   |                     | CZ 20031622 A3             | 15-10-2003          |
|   |   |                     | WO 0244281 A1              | 06-06-2002          |
|   |   |                     | EP 1358270 A1              | 05-11-2003          |
|   |   |                     | NO 20032463 A              | 17-07-2003          |
|   |   |                     | SK 8352003 A3              | 07-10-2003          |
|   |   |                     | TW 548314 B                | 21-08-2003          |
| EP 1348737                                | A | 01-10-2003          | EP 1348737 A1              | 01-10-2003          |
|   |   |                     | WO 03082985 A1             | 09-10-2003          |

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**